



## Scientific investigation into the water sensitivity of twentieth century oil paints



Judith Lee<sup>a,\*</sup>, Ilaria Bonaduce<sup>b</sup>, Francesca Modugno<sup>b</sup>, Jacopo La Nasa<sup>b</sup>,  
Bronwyn Ormsby<sup>a</sup>, Klaas Jan van den Berg<sup>c</sup>

<sup>a</sup> Conservation Department, Tate, Millbank, London SW1P 4RG, United Kingdom

<sup>b</sup> Department of Chemistry and Industrial Chemistry, University of Pisa, via Moruzzi 13-56124, Pisa, Italy

<sup>c</sup> Cultural Heritage Agency of the Netherlands (RCE), Hobbemastraat 22, 1071, ZC, Amsterdam

### ARTICLE INFO

#### Article history:

Received 31 August 2017

Received in revised form 19 December 2017

Accepted 12 January 2018

Available online xxx

#### Keywords:

Water sensitivity

Modern oil paintings

Electrospray ionisation mass spectrometry

Gas chromatography–mass spectrometry

Liquid chromatography–mass spectrometry

Principal component analysis

### ABSTRACT

In order to develop a better understanding at the molecular level of water sensitivity in twentieth century oil paintings, water sensitive Winsor & Newton oil paint swatches and twentieth century oil paintings were characterised using gas chromatography–mass spectrometry (GC–MS) and direct injection electrospray ionisation mass spectrometry (ESI–MS), and the data were analysed using principal component analysis. Liquid chromatography coupled with tandem mass spectrometry based on quadrupole and time of flight mass detectors and electrospray interface (HPLC–ESI–Q–ToF) was also used to obtain a better insight into the molecular composition of a selection of samples. The study highlights a strong relationship between the molecular composition of the binding medium and the type of pigment present in the paint, which relates to water sensitivity. Consistently non-water sensitive lead white, titanium white, and zinc white paints [all containing zinc oxide] contained a relatively low proportion of extractable diacids, and a relatively high proportion of extractable short chain monoacids. These paints also contained a relatively low level of unsaturated and hydroxylated glycerides. Water sensitive iron oxide and ultramarine paints are associated with both a relatively high degree of oxidation and a high proportion of extractable diacids, as well as a relatively high content of unsaturated and hydroxylated glycerides. Water sensitive cadmium red, yellow and orange paints were generally not highly oxidised, but they also contained a relatively high content of unsaturated and hydroxylated glycerides. It is hypothesised that water sensitivity relates to a low degree of saponification and crosslinking and possibly, on the relative content of dicarboxylic acids.

© 2018 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

### 1. Introduction

The phenomena of the water sensitivity of twentieth century oil paintings is of concern to conservators since it can complicate or prevent surface cleaning treatment and consolidation [1]. There are many examples of water sensitive unvarnished twentieth century oil paintings reported in the literature including works by Karel Appel, Jasper Johns, Robyn Denny, Wassily Kandinsky, Kazimir Malevich, Piet Mondrian, Clyfford Still, Paula Rego, Patrick Heron, Francis Bacon and Per Kerkeby [1–5]. There is currently a need to develop an understanding at the molecular level of the characteristics and causes of water sensitivity in twentieth century oil paintings in order to inform the development of suitable materials and methodologies for surface cleaning [6]

as well as potentially limiting the development of water sensitivity in paints. This is critical in order to ensure that water sensitive modern oil paintings will be in a condition fit for display in the medium to long term.

There are many causal factors that are believed to be implicated in the development of water sensitivity in twentieth and twenty first century oil paintings [7]:

- modern oil paint formulation including the choice of pigment, binder, extender and additives such as metal soaps and driers
- environmental conditions such as relative humidity, UV light and atmospheric pollutants
- artists' use and modification of commercially prepared materials

The conversion of magnesium carbonate [an extender used by Winsor & Newton (W&N)] to form water soluble magnesium sulphate heptahydrate upon exposure to environmental SO<sub>2</sub> is one known cause of water sensitivity in modern oil paintings [8]. In addition, a

\* Corresponding author.

E-mail addresses: [judith.lee@tate.org.uk](mailto:judith.lee@tate.org.uk) (J. Lee), [ilaria.bonaduce@unipi.it](mailto:ilaria.bonaduce@unipi.it) (I. Bonaduce), [francesca.modugno@unipi.it](mailto:francesca.modugno@unipi.it) (F. Modugno), [jacopo.lanasa@for.unipi.it](mailto:jacopo.lanasa@for.unipi.it) (J. La Nasa), [bronwyn.ormsby@tate.org.uk](mailto:bronwyn.ormsby@tate.org.uk) (B. Ormsby), [K.van.den.Berg@cultureelerfgoed.nl](mailto:K.van.den.Berg@cultureelerfgoed.nl) (K.J. van den Berg).

high dicarboxylic acid content has been observed in some water sensitive oil paint samples [9] suggesting that the composition of the binding medium may relate to water sensitivity.

Artists' oil paints are typically made using drying oils and semi-drying oils such as linseed, poppy and safflower oil [9]. Drying oils - which are initially comprised of triglycerides containing saturated and polyunsaturated fatty acids - cure via a complex process based on autoxidative radical chain reactions [10]. The first step of curing is the abstraction of a hydrogen free radical, followed by oxygen addition, leading to the formation of a peroxide. A peroxide can evolve through two main pathways, in competition with one another, one leading to polymerisation, and one leading to oxidative scission [7] which results in the formation of  $\alpha,\omega$ -dicarboxylic acids as final products [11]. Nonanedioic (azelaic) acid along with octanedioic (suberic) and decanedioic (sebacic) acids are the major diacids produced as a result of oxidative scission. The hydrolysis of ester bonds that occurs upon ageing results in the formation of diglycerides, monoglycerides, free fatty acids and diacids, as well as glycerol [12]. Certain cations contained in pigments and extenders, including lead, zinc, copper, cobalt, etc., are able to form metal soaps with carboxylic moieties produced by oxidation and hydrolysis [13,14].

In this study the relationship between the molecular composition of the binding medium and water sensitivity was further investigated. Samples taken from W&N artists' oil paint swatches (samples painted out by the manufacturer during production to monitor drying behaviour) dating from 1945 to 2003 and naturally aged since then and samples from a wide series of case study twentieth century oil paintings were analysed using a combination of Fourier transform infrared spectroscopy (FTIR), gas chromatography-mass spectrometry (GC-MS), direct injection electrospray ionisation mass spectrometry (ESI-MS), and liquid chromatography coupled with tandem mass spectrometry based on quadrupole and time of flight mass detectors and electrospray interface (HPLC ESI-Q-ToF). These techniques have been successfully used for the analysis of lipid binding media [15–19]. Sample preparation for GC-MS typically involves extraction of lipids, hydrolysis of glycerides and metal soaps, and derivatisation to increase the volatility of extracted compounds [20]. In this case (*m*-trifluoromethylphenyl) trimethylammonium hydroxide (TMTFTH) in methanol was used as a one-step derivatisation (transesterification/methylation) agent (Meth Prep II) [21,22] that does not require complex sample pre-treatments or extraction steps and therefore minimises loss of sample, and the risk of contamination [23]. When applied to oil paint samples, TMTFTH converts non-crosslinked fatty acids and diacids originally present as glycerides, as metal soaps or as free fatty acids into the corresponding methyl esters [21], giving information on the whole organic content, with the exception of the crosslinked polymeric network. Direct injection electrospray ionisation mass spectrometry (ESI-MS) was used to analyse the ethanol extracts of the paint samples. This, in combination with the fact that data used were acquired in the negative mode, allowed the gathering of information on the most polar and soluble constituents of the paints, including free fatty acids and dicarboxylic acids, as well as non-crosslinked glycerides containing at least a dicarboxylic acid. Liquid chromatography coupled with ESI-Q-ToF mass spectrometry (HPLC ESI-Q-ToF), was used to evaluate the glyceride profile from a qualitative and semi-quantitative point of view [19]. Finally, multivariate analysis was used to support data interpretation, allowing the identification of trends in the large data set as well as differences between water sensitive and non-water sensitive samples.

## 2. Materials and methods

### 2.1. Samples

Winsor and Newton (W&N) produced paint swatches to monitor the drying behaviour of each batch of manufactured paint. Samples of paint were applied to primed canvas or a paper support (using a palette knife or draw-down bar). A group of 27 water sensitive and non-water

sensitive naturally aged W&N Artists' Oil Colour swatches dating from 1945 to 2003 (see Table 1) were selected. Their water sensitivity was evaluated with an established swab rolling method [3] and the basic paint composition of the investigated W&N swatches is published in detail elsewhere [24]. In addition to the paint swatches, a total of 86 non-water sensitive and water sensitive samples were taken from selected case study paintings as listed in Table 2. The composition of the samples (i.e., pigment, binding media and extender) removed from case study paintings is shown in Supplementary data, Table A.1.

### 2.2. Fourier transform infrared spectroscopy (FTIR)

Transmission FTIR spectroscopic analysis was carried out on a Thermo scientific Nicolet iN10 MX microscope using a single diamond cell. 64 scans were collected at a resolution of  $4\text{ cm}^{-1}$  across a wavenumber range of 4000 to  $600\text{ cm}^{-1}$ . Data was processed using Omnic 8 software.

### 2.3. Electrospray ionisation mass spectrometry (ESI-MS)

Direct injection ESI-MS analyses were carried out on paint samples of 0.1–0.5 mg after solvent extraction using ethanol [25]. The extract was mixed 1:1 with 20 mM ammonium acetate ( $\text{NH}_4\text{Ac}$ ) in ethanol. Samples were delivered to the MS system with a Micromass CapLC system: MS analysis was carried out with a Micromass Q-tof-2, equipped with a nano probe and ESI source. MS data were collected and interpreted using MassLynx 4.0 software (Waters). All spectra were collected in high mass resolution mode. Since the molecular formula of the ions is unambiguous for all ions in this study, only nominal masses are presented.

### 2.4. Gas chromatography-mass spectrometry (GC-MS)

Two surface scrapings (of <1 mg) and two bulk samples (of around 1 mg) were taken from each W&N swatch. Surface samples only were taken from case study paintings. Samples were derivatised using Meth Prep II (Grace™ Alltech™). Details on the analytical procedure are reported elsewhere [22]. GC was carried out on a Varian CP-3900 GC coupled with a 1200L MS detector. Oven program:  $80\text{ }^\circ\text{C}$  ramped to  $320\text{ }^\circ\text{C}$  at  $10\text{ }^\circ\text{C}/\text{min}$  then held for 5 min at  $320\text{ }^\circ\text{C}$ . Total run time was 29 min. Split (20:1) injection volume was  $1\text{ }\mu\text{L}$ , and the helium flow was  $1.0\text{ mL}/\text{min}$ . MS conditions: source temperature:  $220\text{ }^\circ\text{C}$ ; transfer line temperature:  $270\text{ }^\circ\text{C}$ , injection port set at  $300\text{ }^\circ\text{C}$ . Column: Phenomenex Zebron ZB-5 column (30 m length;  $0.25\text{ mm i.d.}$ ;  $0.25\text{ }\mu\text{m}$  film thickness). EI mode (70 eV); scan group 1: 45–300 amu; Group 2: 45–700 amu at 16 mins, every 1 s. Chromatographic peak areas were used to calculate ratios between the abundances of significant analytes.

### 2.5. HPLC-ESI-Q-ToF

For the HPLC-ESI-Q-ToF analyses samples (2–3 were subjected to extraction assisted by microwaves in a microwave oven Ethos One (Milestone, U.S.A.) (power 600 W), with  $300\text{ }\mu\text{L}$  of a chloroform-hexane (3:2) mixture at  $80\text{ }^\circ\text{C}$  for 25 min. The extracts were dried under a nitrogen stream, diluted with  $600\text{ }\mu\text{L}$  of elution mixture, and filtered on a  $0.45\text{ }\mu\text{m}$  PTFE filter (Grace Davison Discovery Sciences, U.S.A.) just before injection.

HPLC-ESI-Q-ToF analyses were carried out using a 1200 Infinity HPLC, coupled with a Quadrupole-Time of Flight tandem mass spectrometer 6530 Infinity Q-ToF detector by a Jet Stream ESI interface (Agilent Technologies). The chromatographic separation was carried out using a Poroshell 120 EC-C18 column ( $3.0\text{ mm} \times 5.0\text{ mm}$ ,  $2.7\text{ }\mu\text{m}$  particle size) with a Zorbax eclipse plus C-18 guard column ( $4.6\text{ mm} \times 12.5\text{ mm}$ ,  $5\text{ }\mu\text{m}$  particle size) at a flow rate of  $0.3\text{ mL}\cdot\text{min}^{-1}$  and at  $45\text{ }^\circ\text{C}$ . Aliquots of  $10\text{ }\mu\text{L}$  were injected and the elution gradient was

Download English Version:

<https://daneshyari.com/en/article/7640978>

Download Persian Version:

<https://daneshyari.com/article/7640978>

[Daneshyari.com](https://daneshyari.com)